

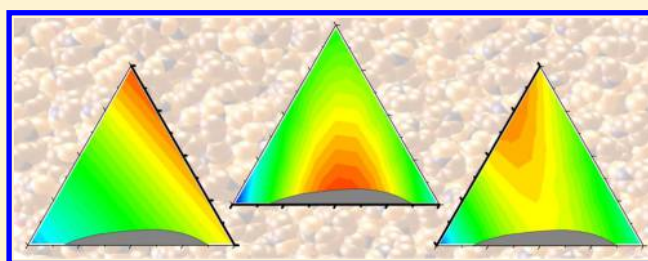
# Diffusion Coefficients of a Highly Nonideal Ternary Liquid Mixture: Cyclohexane–Toluene–Methanol

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## Supporting Information

**ABSTRACT:** To better understand diffusion phenomena in highly nonideal ternary liquid mixtures, cyclohexane–toluene–methanol is studied by equilibrium molecular dynamics (EMD) simulation. Intradiffusion and Maxwell–Stefan (MS) diffusion coefficients, being strictly kinetic properties, are predicted by EMD over the entire composition range at ambient conditions. The thermodynamic contribution to the Fick diffusion coefficients is studied with an excess Gibbs energy model. Predictive results from the combination of these two approaches are in convincing agreement with experimental Fick diffusion coefficient data. Different aspects determining the composition dependence of diffusion coefficients, such as their behavior at the binary limits, hydrogen bonding, and stability criteria, are discussed. While the intradiffusion coefficients exhibit only a weak composition dependence, the MS diffusion coefficients are strongly affected by the nonideality of the present mixture. Fick diffusion coefficients reveal pronounced diffusive coupling effects and are mainly governed by the thermodynamic contribution, especially in the vicinity of the miscibility gap.



## INTRODUCTION

The knowledge of composition-dependent diffusion coefficients is essential for understanding and modeling various mass-transfer processes, like absorption, evaporation, or liquid–liquid extraction.<sup>1–5</sup> An extensive amount of research was conducted on the estimation, interpretation, and prediction of diffusion coefficients for binary liquid mixtures.<sup>6–11</sup> However, most mixtures appearing in nature and technical applications are multicomponent. Little experimental data are available for ternary or higher mixtures because of their much more complex diffusion behavior compared to binary mixtures.<sup>12–15</sup> One reason are coupled diffusion effects where a gradient of one species induces a diffusive flux of another species. The lack of a broad experimental database impedes the development and verification of predictive equations or correlations for multicomponent mixtures.<sup>16,17</sup>

Molecular modeling and simulation was successfully applied by our group to predict diffusion coefficients of binary<sup>10,11,18</sup> and ternary<sup>19–21</sup> liquid mixtures. In this work, equilibrium molecular dynamics (EMD) simulation was used to investigate different diffusion coefficients, i.e., intradiffusion, Maxwell–Stefan (MS) and Fick diffusion coefficients, of a highly nonideal ternary mixture: cyclohexane–toluene–methanol. It appears particularly interesting because (1) it exhibits a miscibility gap at ambient conditions; (2) a large experimental database on the Fick diffusion coefficients is available in the literature;<sup>22–24</sup> (3) it is composed of small molecules, which can be modeled without internal degrees of freedom, limiting the computational effort; (4) it was investigated by the Diffusion Coefficients in Mixtures (DCMIX) project, for which experiments were conducted aboard the International Space Station.<sup>25,26</sup>

The aims of this study are to clarify the composition-dependent behavior of isothermal–isobaric diffusion coefficients of a ternary mixture with a miscibility gap and to further validate the capabilities of EMD simulation for predicting diffusion coefficients of multicomponent mixtures. Furthermore, the interrelations between intradiffusion, MS and Fick diffusion coefficients are discussed together with constraints and limitations of the Fick diffusion coefficient matrix, resulting from the liquid–liquid equilibrium (LLE) phase separation and the binary subsystems. For this purpose, the entire composition range of the ternary mixture was studied, cf. Figure 1.

## DIFFUSION COEFFICIENTS

Three types of diffusion coefficients are nowadays usually discussed in the literature and used for scientific and engineering calculations, i.e., intradiffusion (often also called self-diffusion) coefficients, MS diffusion coefficients, and Fick diffusion coefficients.

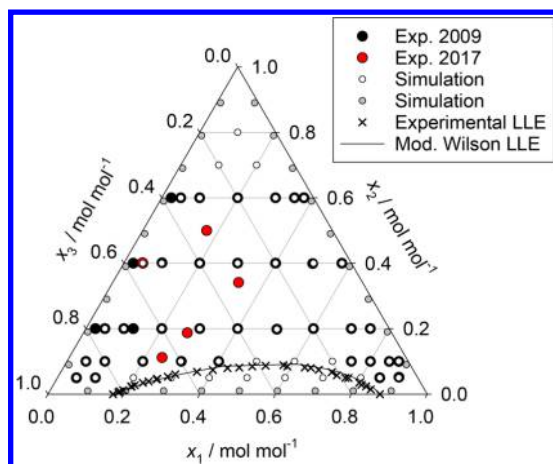
The microscopic description of intradiffusion coefficients originated in Einstein's formulation of Brownian motion,<sup>28</sup> which assumes the random motion of particles suspended in a fluid is a consequence of interactions with the molecules of the fluid. This concept can be transferred to the molecules of a pure fluid or mixture to describe their mobility in the absence of diffusive driving force gradients. This mobility is quantified by the intradiffusion coefficient  $D_i$  of species  $i$  which is related

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**Figure 1.** Compositions of cyclohexane (1)–toluene (2)–methanol (3) for which experimental diffusion coefficients are available,<sup>22–24</sup> state points studied in this work (white bullets, intradiffusion and MS coefficients; gray bullets, only intradiffusion coefficients), as well as experimental LLE compositions<sup>27</sup> and modified Wilson  $g^E$  model at 298.15 K and 0.1 MPa.

to the mean squared displacement of single molecules in terms of the elapsed time

$$D_i = \frac{\langle \Delta r_i^2 \rangle}{6\Delta t} \quad (1)$$

Intradiffusion coefficients of multicomponent mixtures, in contrast to mutual diffusion coefficients, can be measured straightforwardly,<sup>29</sup> for example by nuclear magnetic resonance (NMR) or with the help of labeled tracers of one species.<sup>30</sup> The latter method relies on the fact that the intradiffusion coefficient of a strongly diluted (or tracer) species is equal to a mutual diffusion coefficient, describing diffusion due to a concentration gradient.<sup>31</sup> This relation is also frequently used to model transport diffusion processes only on the basis of intradiffusion coefficients, which raises the question up to which concentration a species can be treated as a diluted one.

According to the theory of irreversible thermodynamics, diffusive fluxes are defined on the basis of the entropy production rate so that isothermal–isobaric transport diffusion is driven by chemical potential gradients.<sup>32</sup> A common model for the description of multicomponent diffusive transport is the MS approach.<sup>33,34</sup> Here, the driving force is expressed in accordance with irreversible thermodynamics by the chemical potential gradients  $\nabla\mu_i$ , which lead to a relative velocity between two components ( $\mathbf{u}_i - \mathbf{u}_j$ ). For a ternary mixture, the MS approach provides three equations

$$\begin{aligned} -\frac{1}{RT}\nabla\mu_1 &= \frac{x_2(\mathbf{u}_1 - \mathbf{u}_2)}{D_{12}} + \frac{x_3(\mathbf{u}_1 - \mathbf{u}_3)}{D_{13}} \\ -\frac{1}{RT}\nabla\mu_2 &= \frac{x_1(\mathbf{u}_2 - \mathbf{u}_1)}{D_{21}} + \frac{x_3(\mathbf{u}_2 - \mathbf{u}_3)}{D_{23}} \\ -\frac{1}{RT}\nabla\mu_3 &= \frac{x_1(\mathbf{u}_3 - \mathbf{u}_1)}{D_{31}} + \frac{x_2(\mathbf{u}_3 - \mathbf{u}_2)}{D_{32}} \end{aligned} \quad (2)$$

with gas constant  $R$ , temperature  $T$ , and three independent MS diffusion coefficients  $D_{ij}$ . The MS diffusion coefficients are, in contrast to the Fick diffusion coefficients, symmetric  $D_{ij} = D_{ji}$ , which is a consequence of the Onsager reciprocal relations

(ORR).<sup>35</sup> Knowledge of the composition-dependent MS diffusion coefficients is essential when MS equations are used, for example to calculate the mass transfer with rate-based approaches.<sup>36</sup> Because these coefficients can not be obtained experimentally, effort is being made to develop models which relate MS to intradiffusion coefficients.<sup>37–40</sup> EMD simulation is a particularly promising method for the prediction of MS diffusion coefficients.

In experimental work on mutual diffusion coefficients, changes of concentrations are usually measured with optical methods, for example, employing a differential refractometer, Gouy interferometer, or Mach–Zehnder interferometer.<sup>41</sup> Thus, the generalized form of Fick's law is used for analysis, which relates molar fluxes to concentration gradients. In the case of a ternary mixture, two molar fluxes  $J_i^v$  are defined in the volume reference frame ( $^v$ ) by

$$\begin{aligned} J_1^v &= -D_{11}^v \nabla C_1 - D_{12}^v \nabla C_2 \\ J_2^v &= -D_{21}^v \nabla C_1 - D_{22}^v \nabla C_2 \end{aligned} \quad (3)$$

with four Fick diffusion coefficients  $D_{ij}^v$  and two molar concentration gradients  $\nabla C_i$ . Here, the molar fluxes are defined relative to a volume-averaged velocity  $\mathbf{u}^v = \sum \phi_i \mathbf{u}_i$ , which is usually assumed to be zero if the excess molar volume is negligible. The flux of the third (reference) component  $J_3^v$  then results from the closure  $\sum \bar{v}_i J_i^v = 0$ , with partial molar volumes  $\bar{v}_i$ . From these equations, it is evident that Fick diffusion coefficients depend on the order of components, which can complicate the comparison of diffusion coefficients of different mixtures.

From a theoretical point of view, it is often more convenient to work with fluxes relative to a molar-averaged velocity  $\mathbf{u} = \sum x_i \mathbf{u}_i$  and assuming mole fraction gradients  $\nabla x_i$  as driving forces. In this case, the Fick diffusion coefficients  $D_{ij}$  are defined in the molar reference frame, which differ from the coefficients in the volume reference frame  $D_{ij}^v$  given in eq 3. Fick diffusion coefficients can be transformed from one reference frame to another; the equations are given in the [Supporting Information](#).

The driving forces are the main difference between the MS and Fick approaches. Gradients of the chemical potentials can be transformed to mole fraction gradients by means of partial derivatives of chemical potentials with respect to mole fractions  $(\partial\mu_i/\partial x_j)_{T,p}$ , which constitute the thermodynamic factor matrix  $\Gamma$ . Thus, MS and Fick diffusion coefficients can also be related to each other through<sup>35</sup>

$$\begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} = \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix}^{-1} \times \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} \quad (4)$$

The elements of matrix  $B$  result from a transformation of the MS eqs 2 to a form of the molar flux equations in the molar reference frame, cf. the [Supporting Information](#) eq S9. Thus, they are related to the MS diffusion coefficients by

$$\begin{aligned} B_{ii} &= \frac{x_i}{D_m} + \sum_{j \neq i=1}^n \frac{x_j}{D_{ij}} \\ B_{ij} &= -x_i \left( \frac{1}{D_{ij}} - \frac{1}{D_m} \right) \end{aligned} \quad (5)$$

where  $n$  is the number of components and also stands for the reference component.

The elements of the thermodynamic factor matrix are defined by<sup>42</sup>

$$\Gamma_{ij} = \frac{x_i}{RT} \frac{\partial \mu_i}{\partial x_j} \bigg|_{T,p,\Sigma} = \delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j} \bigg|_{T,p,\Sigma} \quad (6)$$

with activity coefficients  $\gamma_i$ . The symbol  $\Sigma$  indicates a constraint derivative; that is, it must be carried out while keeping constant the mole fractions of all other species, except for the  $n$ th, such that the mole fractions of all species sum up to unity.

Different constraints are imposed on the Fick diffusion coefficient matrix and can be used to assess the consistency of data. First, all ternary diffusion coefficients in the vicinity of the binary limits must be consistent with the diffusion coefficients of the binary subsystems.<sup>15,22,23</sup> These limiting values do not depend on the reference frame. If one of the first two components is infinitely diluted (e.g.,  $x_1 \rightarrow 0$ ), its own main Fick diffusion coefficient must be the same as its intradiffusion coefficient ( $D_{11} = D_1^\infty$ ), the cross coefficient must approach zero ( $D_{12} = 0$ ), and the second main Fick diffusion coefficient is equivalent with the binary Fick diffusion coefficient between the other two components ( $D_{22} = D_{23}^{\text{bin}}$ ). Analogous relations hold for the second component ( $x_2 \rightarrow 0$ ), and further relations apply for the third component ( $x_3 \rightarrow 0$ ), which can be derived from a change of the order of components, cf. the [Supporting Information](#).

Another important restriction is imposed on the Fick diffusion coefficient matrix by the thermodynamic stability requirement, which can be expressed through the partial derivatives of the chemical potentials.<sup>43,44</sup> For thermodynamic phase stability, the determinant of the thermodynamic factor matrix must be positive; consequently, both eigenvalues must be positive. Note that the eigenvalues of the Fick diffusion matrix are independent of the reference frame. It follows from this constraint that also the Fick diffusion coefficient matrix  $\mathbf{D}$  must have real and positive eigenvalues.<sup>45,46</sup> At the spinodal, at least one eigenvalue  $\hat{D}_i$  is zero, i.e.,  $\det(\mathbf{D}) = \hat{D}_1 \hat{D}_2 = 0$ .<sup>3</sup>

A further constraint is imposed on the Fick diffusion coefficient matrix by the ORR,<sup>47</sup> which are a consequence of the invariance of the microscopic equations of motion under time reversal.<sup>32</sup> Details on the resulting relation between the four Fick diffusion coefficients are given in the [Supporting Information](#).

## ■ COMPUTATION DETAILS

**Molecular Models and Simulation.** In the present EMD simulation work, rigid, united-atom type force field models were used, describing the intermolecular interactions with Lennard-Jones (LJ) potentials, point charges, or point quadrupoles. Their parameters were taken from preceding work on cyclohexane,<sup>48</sup> toluene<sup>11</sup> and methanol.<sup>49</sup> No binary or ternary force field parameters were introduced, specifying the unlike LJ interactions with the Lorentz–Berthelot combining rules, such that all mixture data on kinetic properties are strictly predictive.

The molar density, self-diffusion coefficient, and shear viscosity from the pure component models listed in [Table 1](#) are in adequate agreement with experimental data. The diffusion coefficients of all three binary subsystems were successfully predicted in previous work.<sup>10,11</sup>

Diffusion coefficients were sampled in this work with the Green–Kubo formalism, through which transport coefficients are related to the time integrals of correlation functions of the associated fluxes. The intradiffusion coefficient of species  $i$  was

**Table 1.** Pure Component Molar Density, Self-Diffusion Coefficient, and Shear Viscosity of the Utilized Force Field Models Obtained from EMD Simulation (This Work) Compared with Experimental Data at 298.15 K and 0.1 MPa<sup>a</sup>

	$\rho$ (mol L <sup>-1</sup> )	$D^0$ (10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup> )	$\eta$ (10 <sup>-4</sup> Pa s)	ref
cyclohexane	9.218 (2)	1.561 (3)	7.3 (4)	MD
	9.195	1.47	8.98	50, 51
toluene	9.344 (2)	2.379 (5)	4.8 (3)	MD
	9.358	2.267	5.67	51, 52
methanol	24.541 (6)	2.444 (6)	5.5 (4)	MD
	24.551	2.13	5.52	53, 54

<sup>a</sup>The number in parentheses indicates the statistical uncertainty of the simulation data in the last digit.

calculated from the time integral of the velocity autocorrelation function of single molecules averaged over all  $N_i$  molecules that belong to that species<sup>55</sup>

$$D_i = \frac{1}{3N_i} \int_0^\infty \left\langle \sum_{k=1}^{N_i} \mathbf{v}_i^k(0) \cdot \mathbf{v}_i^k(t) \right\rangle dt \quad (7)$$

Therein,  $\mathbf{v}_i^k(t)$  is the center of mass velocity vector of molecule  $k$  of species  $i$  at some time  $t$ , and the brackets  $\langle \dots \rangle$  denote the ensemble average.

Transport diffusion is related to the collective motion of molecules and can thus be described by phenomenological transport diffusion coefficients which were calculated from the net velocity correlation functions of species  $i$  and  $j$ <sup>56</sup>

$$\lambda_{ij} = \frac{1}{3N} \int_0^\infty \left\langle \sum_{k=1}^{N_i} \mathbf{v}_i^k(0) \cdot \sum_{l=1}^{N_j} \mathbf{v}_j^l(t) \right\rangle dt \quad (8)$$

where  $N$  is the total number of molecules. For a ternary mixture, there are nine phenomenological coefficients that are constrained by  $\lambda_{ij} = \lambda_{ji}$  (ORR) and  $\sum_i M_i \lambda_{ij} = 0$ , resulting from dependent molar fluxes in the mass reference frame  $\sum_i M_i J_i^m = 0$ , where  $M_i$  stands for molar mass of species  $i$ . The latter condition is fulfilled during the EMD simulations within machine error because the net momentum is set to zero at the beginning of a simulation. Concerning the ORR, an average deviation of 11% between  $\lambda_{ij}$  and  $\lambda_{ji}$  was determined. Consequently, for further calculations, a mean value of the coefficients was used, i.e.,  $(\lambda_{ij} + \lambda_{ji})/2$ . Consequently, the phenomenological coefficients can be transformed to only three independent MS diffusion coefficients with [eq 5](#) and<sup>56</sup>

$$\Delta_{ij} = \left( \frac{\lambda_{ij}}{x_j} - \frac{\lambda_{in}}{x_n} \right) - x_i \left( \sum_k \frac{\lambda_{kj}}{x_j} - \sum_k \frac{\lambda_{kn}}{x_n} \right) \quad (9)$$

$$\Delta = \mathbf{B}^{-1}$$

This relation results from the transformation of the different flux equations, which are given in the [Supporting Information](#) as [eq S10](#) and [S13](#).

All EMD simulation runs were carried out with the program *ms2*.<sup>57–59</sup> A cubic volume was assumed with periodic boundary conditions containing 4000 molecules. Intermolecular interactions were explicitly evaluated within 17.5 Å, considering the LJ long-range corrections analytically beyond the cutoff radius with the angle-averaging method of Lustig<sup>60</sup> and the long-range electrostatic interactions by means of the reaction field method.<sup>61</sup> Simulations were conducted in the canonic (NVT) ensemble, where the temperature was controlled by velocity



Table 2. Modified Wilson  $g^E$  Model Parameters

comp. $i$	comp. $j$	$a_{ij}/K$	$a_{ji}/K$	ref.
cyclohexane	toluene	61.62	89.17	VLE fit <sup>64</sup>
toluene	methanol	−150.95	938.03	VLE fit <sup>64</sup>
cyclohexane	methanol	58.403	1019.7	LLE fit <sup>65</sup>

ternary parameters:  $\Lambda_i = 0$

scaling.<sup>55</sup> The simulations were first equilibrated over  $4 \times 10^5$  time steps, followed by production runs of  $4\text{--}5 \times 10^7$  time steps. Newton's equations of motion were solved with a fifth-order Gear predictor-corrector numerical integrator and an integration time step of  $\sim 1$  fs. The intradiffusion as well as the phenomenological diffusion coefficients were calculated by evaluating the center of mass velocities of the molecules every fifth time step and by averaging up to  $4.9 \times 10^5$  independent time origins of the correlation functions with a sampling length of 10 ps for the individual correlation functions.

To obtain reliable simulation results for diffusion coefficients, it is important to carefully consider the system size as well as the length of the correlation functions.<sup>62,63</sup> Exemplary integrated correlation functions considering these two aspects are discussed in the [Supporting Information](#).

**Excess Gibbs Energy Model.** The thermodynamic factor was calculated in this work with a modified Wilson excess Gibbs energy ( $g^E$ ) model,<sup>64</sup> which in contrast to the original Wilson model is capable of describing a miscibility gap. It was already discussed for the binary subsystem cyclohexane–methanol that the predicted Fick diffusion coefficients are very sensitive to the utilized  $g^E$  model as well as to its parameters.<sup>10</sup> For the binary subsystem with LLE phase separation, i.e., cyclohexane–methanol, none of the considered models (Van Laar, Margules, NRTL, UNIQUAC, or modified Wilson) were capable of correctly describing the composition dependence of the activity coefficients, i.e., activity coefficients at infinite dilution (ACID), binodal and spinodal compositions, while the modified Wilson model showed the best results.<sup>10</sup>

The modified Wilson model<sup>64</sup> defines the dimensionless excess Gibbs energy  $Q = g^E/(RT)$  by

$$Q = -\sum_i x_i \ln \left( \frac{\sum_j x_j \Lambda_{ij}}{\sum_k x_k (v_k/v_i)} \right) - \sum_i x_i \ln(\Lambda_i x_m x_n) \quad (10)$$

comprising ternary parameters  $\Lambda_i$  and binary parameters

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp(-a_{ij}/T) \quad (11)$$

with molar volume  $v_i$  of the pure component  $i$  and binary interaction parameters  $a_{ij}$ .

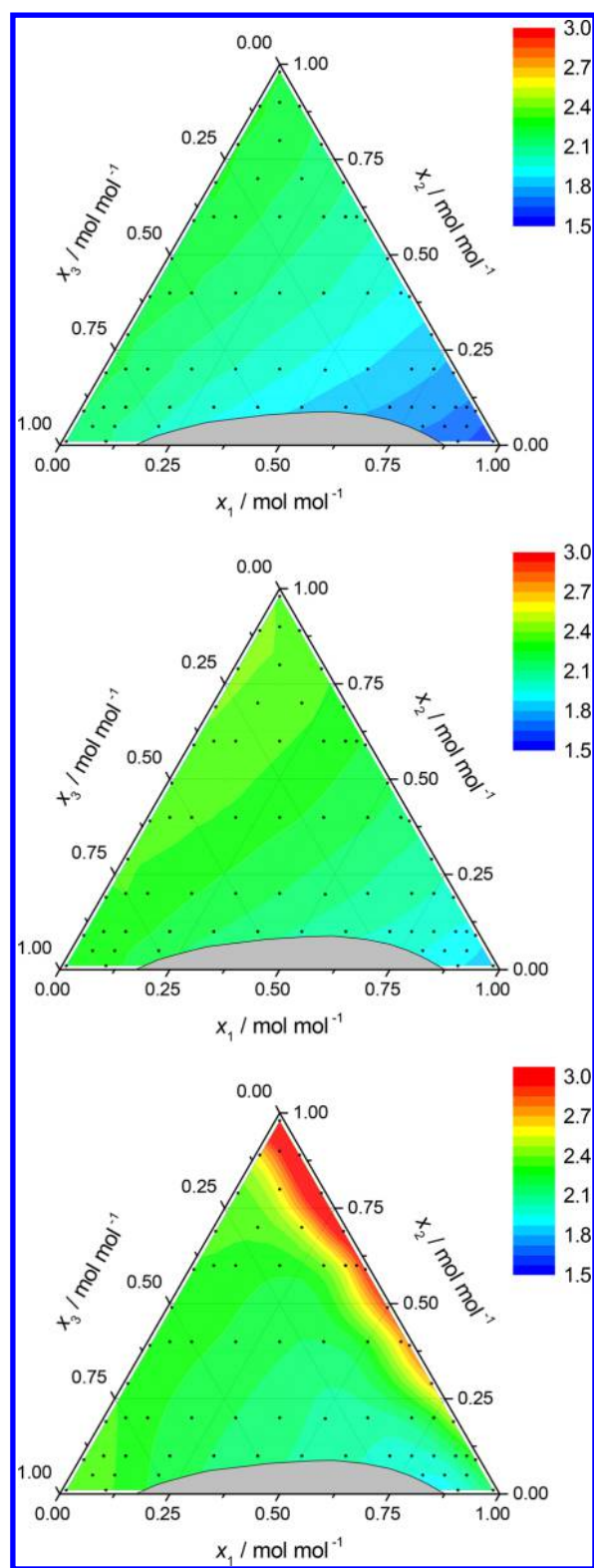
The elements of the thermodynamic factor matrix can be calculated from second-order partial derivatives of  $Q$  with respect to the mole fractions  $x_i$  from<sup>42</sup>

$$\Gamma_{ij} = \delta_{ij} + x_i \left[ Q_{ij} - Q_{in} - \sum_{k=1}^n x_k (Q_{kj} - Q_{kn}) \right] \quad (12)$$

with

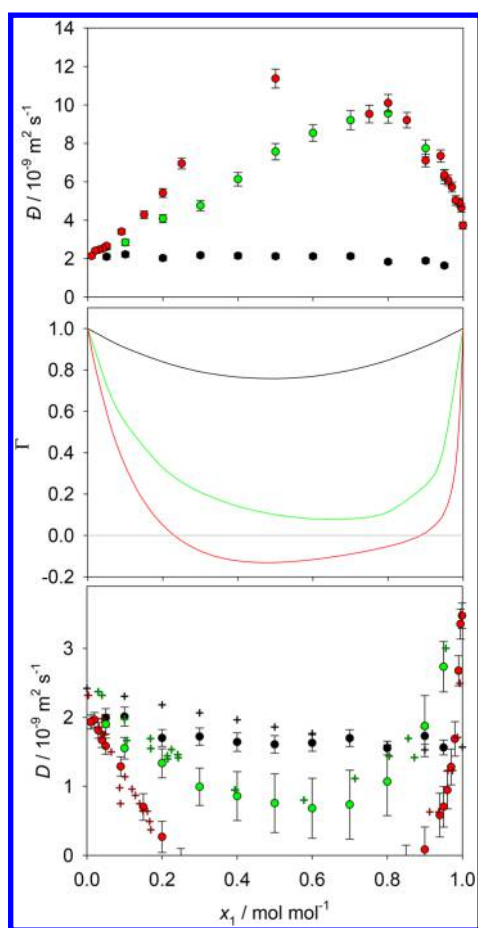
$$Q_i = \frac{\partial Q}{\partial x_i} \bigg|_{x_{k \neq i}}, \quad Q_{ij} = \frac{\partial Q_i}{\partial x_j} \bigg|_{x_{k \neq j}} \quad (13)$$

Note that these are unconstrained partial derivatives, which have to be evaluated while keeping the mole fractions of all other components constant, i.e., not using the constraint  $\sum x_i = 1$ .



**Figure 2.** Intradiffusion coefficients  $D_i$  (in  $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) of cyclohexane (top), toluene (center), and methanol (bottom) in their ternary mixture at 298.15 K and 0.1 MPa.

For the two fully miscible subsystems cyclohexane–toluene and toluene–methanol, model parameters were fitted to experimental vapor–liquid equilibrium (VLE) data.<sup>64</sup> For the subsystem cyclohexane–methanol, two different parameter sets were tested, fitted either to binary LLE data or ACID.<sup>10</sup>



**Figure 3.** Binary subsystems cyclohexane–toluene (black), toluene–methanol (green), and cyclohexane–methanol (red): MS diffusion coefficient from MD simulation (top), thermodynamic factor from modified Wilson  $g^E$  model (center), and resulting Fick diffusion coefficient  $D = \bar{D}\Gamma$  (bottom) are compared with experimental literature data (crosses).<sup>8,20,66–68</sup>

Ternary parameters were either taken from the LLE fit ( $\Lambda_1 = 0.4926$ ,  $\Lambda_2 = 0.3695$ , and  $\Lambda_3 = 0.1569$ )<sup>64</sup> or set to zero. All parameters were fitted to experimental data at about 298.15 K and thus are expected to be valid only close to this temperature. Because no pressure dependence is contained in the  $g^E$  model, the parameters are valid only for low pressures. Pure fluid experimental data were taken for the required molar volumes, cf. Table 1.

For the binary subsystem cyclohexane–methanol, the ACID fit had the best performance to predict the Fick diffusion coefficient in combination with EMD simulation results.<sup>10</sup> In the case of the ternary mixture, the best agreement with experimental Fick diffusion coefficient data was obtained with the LLE fit for cyclohexane–methanol and with ternary parameters set to zero. Thus, these parameters were used in this work and are listed in Table 2. Exemplary results with different parameter sets are given in the Supporting Information.

## RESULTS AND DISCUSSION

**Intradiffusion.** Intradiffusion coefficients can be interpreted as the mobility of molecules of a given species in a mixture in the absence of diffusive driving force gradients. Simulation results for the three intradiffusion coefficients of cyclohexane (1)–toluene (2)–methanol (3) at ambient conditions are shown in Figure 2. All components have similar intradiffusion coefficients of  $2.0\text{--}2.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  in most of the composition range. The intradiffusion coefficient of cyclohexane exhibits the lowest values of  $\sim 1.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  at high cyclohexane concentrations. This is not surprising because cyclohexane has the lowest self-diffusion coefficient as a pure fluid, cf. Table 1. Almost no composition dependence was observed for the intradiffusion coefficient of toluene; these molecules are slightly slower only at high cyclohexane content. The notably smaller methanol molecules have a similar intradiffusion coefficient as toluene or cyclohexane over a wide composition range. This phenomenon can be related to the hydrogen-bonding behavior of methanol molecules, which mostly propagate in associated assemblies and are thus on average slower than methanol monomers. At low methanol mole fractions, fewer methanol molecules have hydrogen-bonded partners and do propagate as monomers so that the intradiffusion coefficient of methanol is significantly higher in this composition range. This interrelation was confirmed by hydrogen-bonding statistics for methanol, which were also sampled by EMD simulation; results are given in the Supporting Information. Another notable observation is that the intradiffusion coefficients of all three components are not affected by the strong thermodynamic nonideality of the present mixture and show no special behavior in the vicinity of the miscibility gap or consolute point.

**Binary Subsystems.** Before discussing ternary mutual diffusion coefficients, it is instructive to review the binary subsystems. Their binary MS diffusion coefficient, thermodynamic factor, and Fick diffusion coefficient are shown in Figure 3.

Cyclohexane–toluene is an almost ideal mixture; because its thermodynamic factor is close to unity. Here, also the MS diffusion coefficient shows only a weak composition dependence and can accurately be predicted on the basis of intradiffusion coefficients with the Darken<sup>69</sup> or Vignes<sup>70</sup> relations, which is not the case for the two other subsystems. Toluene–methanol is highly nonideal, and its thermodynamic factor reaches values close to zero, which is accompanied by a strongly composition-dependent MS coefficient. This coincidence was observed for many binary mixtures of an alcohol and a weakly polar component<sup>11</sup> and can be explained with the clustering behavior of the alcohol molecules, causing strong thermodynamic nonideality and significant deviations of the MS coefficient from the Darken relation through correlated molecular motion.<sup>10</sup> The same phenomenon appears even more pronounced for cyclohexane–methanol so that the thermodynamic factor becomes negative within the miscibility gap. For such binary mixtures with LLE phase separation, a similar composition dependence of the MS diffusion coefficients

**Table 3.** Parameters of Equation 14 Fitted to Present Simulation Data Together with Average Relative Deviations

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	ARD
$D_{12}$	4.140	15.25	18.85	0	0	0	4%
$D_{13}$	−3.227	41.30	82.45	131.22	133.05	505.79	18%
$D_{23}$	6.077	25.70	72.03	−13.458	143.04	218.22	9%

as obtained by EMD simulation is also predicted by local composition models.<sup>71,72</sup>

**Maxwell–Stefan Diffusion Coefficients.** Ternary MS coefficients were sampled over the entire composition range as indicated in Figure 1, but not at very dilute states  $x_i < 0.05 \text{ mol mol}^{-1}$  because the phenomenological coefficients were accompanied by too large statistical uncertainties under such conditions. Numerical results are given in the Supporting Information.

To obtain a good impression of the composition dependence of the three MS coefficients, not perturbed by scattered simulation data, the following polynomial was fitted to simulation data for the ternary mixture and its binary subsystems

$$\bar{D}_{ij} = a + bx_1 + cx_2 + dx_1x_2 + ex_2x_3 + fx_1x_3 \quad (14)$$

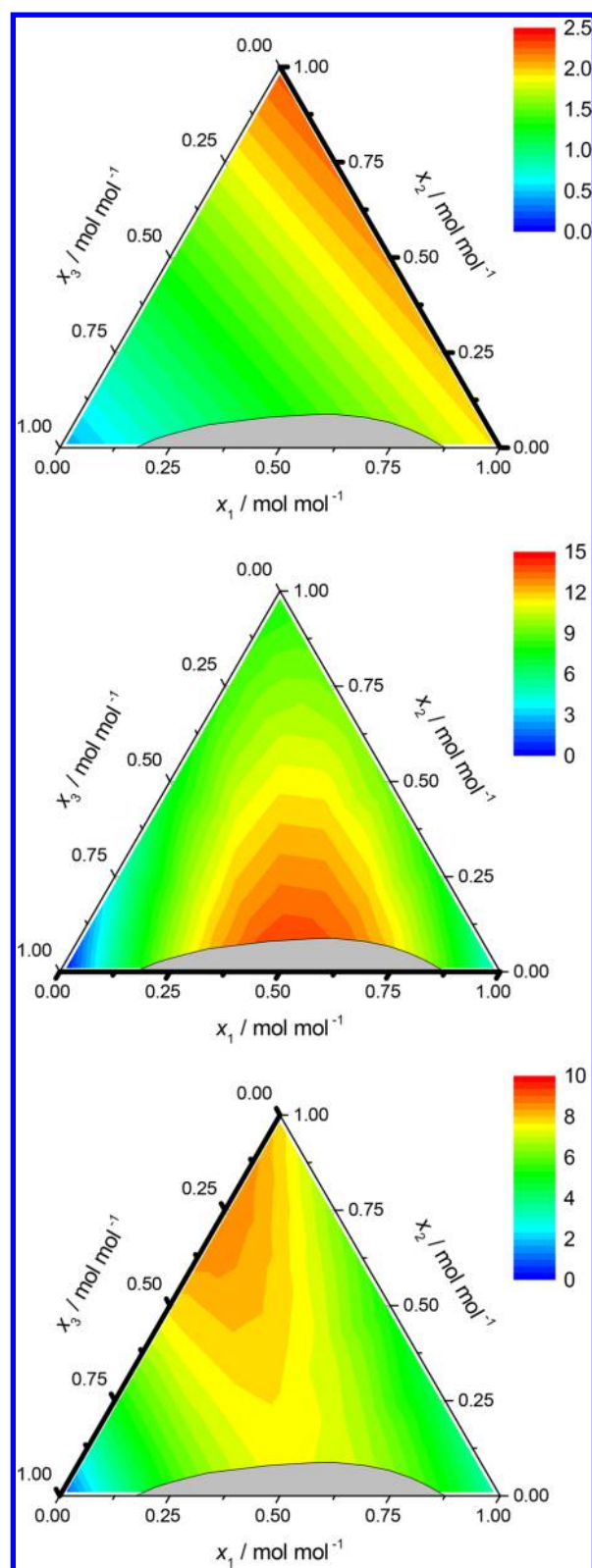
where  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$ , and  $f$  are empirical parameters. These parameters are listed in Table 3, and the resulting MS coefficients are shown in Figure 4. Note that the scale for each of the MS coefficients is different in Figure 4.

In the binary limit  $x_n \rightarrow 0$ , the ternary MS coefficient  $\bar{D}_{ij}$  must coincide with the binary MS coefficient  $\bar{D}_{ij}^{\text{bin}}$ . This requirement is fulfilled by the ternary simulation results and correlation 14, as can be seen when comparing the ternary  $\bar{D}_{ij}$  in the binary limit (indicated by a bold line in Figure 4) with the binary MS coefficients in Figure 3. An additional figure of ternary MS coefficients  $\bar{D}_{ij}$  near that limit at  $x_n = 0.1 \text{ mol mol}^{-1}$  in comparison with binary MS coefficients is presented in the Supporting Information.

In the case of a binary system in the infinite dilution limit  $x_i \rightarrow 0$ ,  $\bar{D}_{ij}^{\text{bin}}$  coincides with the intradiffusion coefficient  $D_i$  of the diluted component. Such an unambiguous assignment can not be made for the behavior of ternary  $\bar{D}_{ij}$  data in the limit  $x_i \rightarrow 0$  and  $x_j \rightarrow 0$ , i.e.,  $x_n \rightarrow 1$ . MS coefficient  $\bar{D}_{12}$  is most reliable to be considered toward this limit because it has the lowest statistical uncertainties, which are a consequence of nearly ideal mixture behavior of cyclohexane–toluene. Values for  $\bar{D}_{12}$  in the limit  $x_3 \rightarrow 1$  are below  $10^{-9} \text{ m}^2 \text{ s}^{-1}$ , which is notably smaller than all three intradiffusion coefficients in this composition range. It can be supposed that such limiting values for MS coefficients can not be obtained from intradiffusion coefficients as discussed, for example, by Liu et al.<sup>73</sup>

The other two MS coefficients  $\bar{D}_{13}$  and  $\bar{D}_{23}$  are accompanied by strong nonidealities and consequently strong fluctuations during molecular dynamics sampling, leading to large statistical uncertainties. Here, the smallest values of  $\sim 2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  also occur in the limit  $x_3 \rightarrow 1$ , which is in agreement with the limiting values of the binary subsystems and intradiffusion coefficients. The highest values of the ternary MS coefficients are given near the binary subsystems at the same compositions for which the binary coefficients exhibit a maximum, i.e. for  $\bar{D}_{13}$  at  $x_1 \sim 0.5 \text{ mol mol}^{-1}$  and for  $\bar{D}_{23}$  at  $x_1 \sim 0.25 \text{ mol mol}^{-1}$ . In the limit opposite to the binary subsystem  $ij$  ( $x_n \rightarrow 1$ ), both coefficients  $\bar{D}_{13}$  and  $\bar{D}_{23}$  are  $\sim 6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , still show strong nonidealities, and have approximately twice the magnitude of the largest intradiffusion coefficient in this region. The knowledge of such nonideal behavior of MS coefficients is important when mass-transfer processes are described with the MS approach.

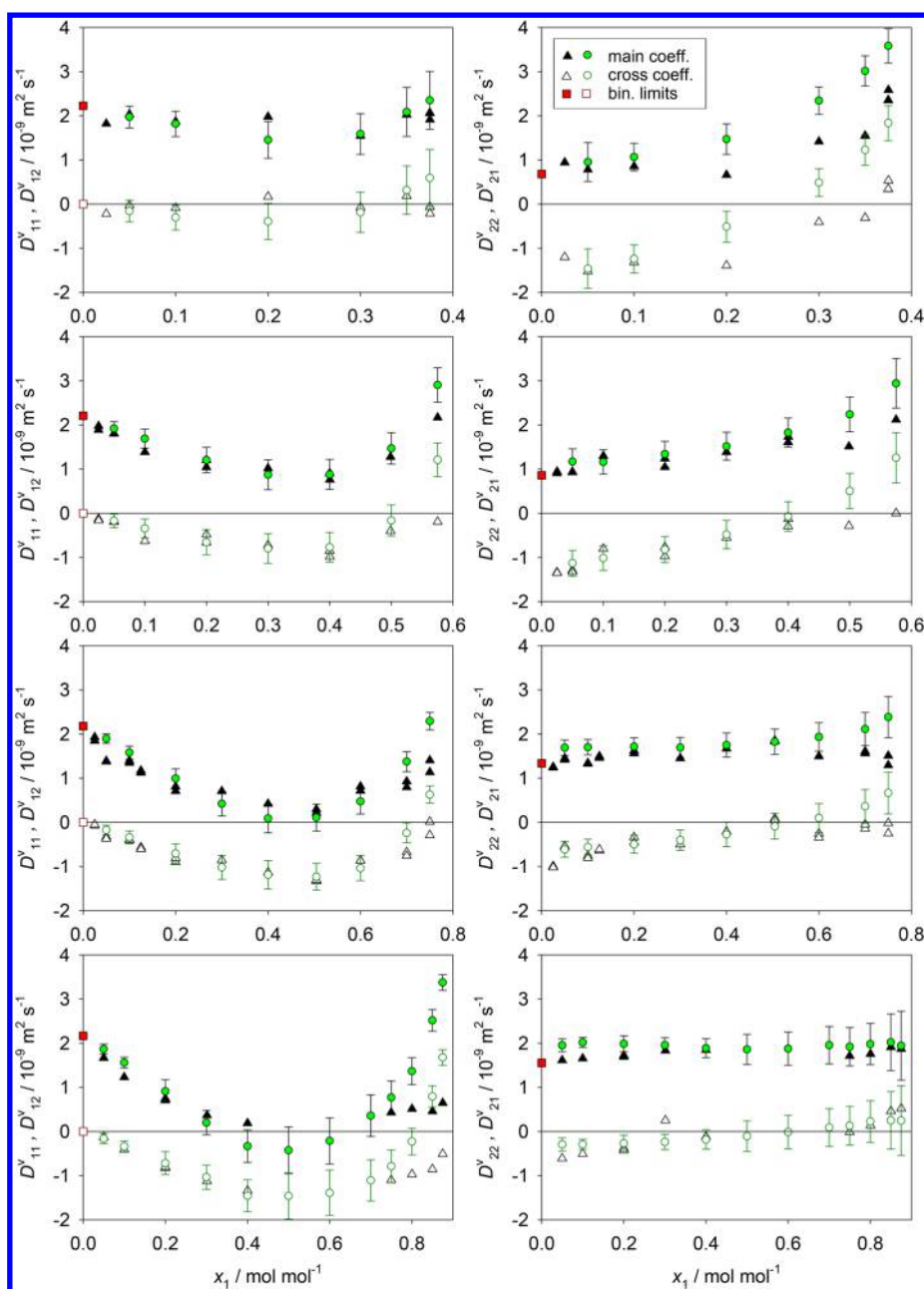
Like for the binary subsystems, it is evident that the composition dependence of ternary MS coefficients can not be predicted with the well-known Darken model. This shortcoming was already discussed by Liu et al.<sup>74</sup> for the nonideal mixture chloroform–acetone–methanol.



**Figure 4.** MS diffusion coefficients  $\bar{D}_{12}$  (top),  $\bar{D}_{13}$  (center), and  $\bar{D}_{23}$  (bottom) (in  $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) of the ternary mixture cyclohexane (1)–toluene (2)–methanol (3). Bold lines indicate the binary limit ( $x_n \rightarrow 0$ ) for  $\bar{D}_{ij}$ .

Furthermore, it was observed that the elements of matrices  $\Delta$  and  $\Gamma$  exhibit an opposing composition dependence; that is, where  $\Delta_{ij}$  have a maximum,  $\Gamma_{ij}$  have a minimum. Ternary plots are given in the Supporting Information. This coincidence is in





**Figure 5.** Fick diffusion coefficients (volume reference frame) of cyclohexane (1)–toluene (2)–methanol (3) at a constant mole fraction of toluene  $x_2 = 0.6 \text{ mol mol}^{-1}$  (first row),  $x_2 = 0.4 \text{ mol mol}^{-1}$  (second row),  $x_2 = 0.2 \text{ mol mol}^{-1}$  (third row), and  $x_2 = 0.1 \text{ mol mol}^{-1}$  (fourth row). Simulation data (circles) and binary limiting values from simulation (squares) are compared with experimental data<sup>22,23</sup> (triangles).

agreement with the behavior observed for thermodynamic factor and MS coefficient of the binary subsystems. It can be related to the microscopic structure of the mixture, i.e., cluster formation, which causes thermodynamic nonideality as well as kinetic nonideality through correlated molecular motion.

Allie-Ebrahim et al.<sup>40</sup> recently proposed a local mole fraction model for the prediction of multicomponent MS coefficients of highly nonideal ternary systems. This model was tested for the present mixture, but it was found that it is not able to predict the strong nonideality of the MS coefficients. Exemplary results are shown in the [Supporting Information](#). Nevertheless, the model of Allie-Ebrahim et al.<sup>40</sup> together with the thermodynamic factor gives overall reasonable results for the Fick diffusion coefficients, which are mainly governed by the thermodynamic contribution, if appropriate  $g^E$  model parameters are used.

**Fick Diffusion Coefficients.** Fick diffusion coefficients are a composite of kinetic and thermodynamic contributions, cf. eq 4. The kinetic part results from velocity correlation functions, i.e., the MS diffusion coefficients. The thermodynamic part, i.e., thermodynamic factor, was calculated with the modified Wilson  $g^E$  model. For highly nonideal ternary mixtures, the composition dependence of Fick coefficients is mainly governed by the thermodynamic contribution; thus, an appropriate combination of model and parameters is essential. Parameters fitted only to binary VLE and LLE data showed the best results and were used to predict ternary Fick diffusion coefficients. Results in the volume reference frame along composition paths with a constant toluene mole fraction together with experimental data from the literature are shown in [Figure 5](#). Average relative deviations between predicted and experimental

Fick diffusion coefficients are 0.48, 0.4, 0.36, and  $0.37 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for  $D_{11}$ ,  $D_{12}$ ,  $D_{21}$ , and  $D_{22}$ , respectively.

The main Fick diffusion coefficient of cyclohexane  $D_{11}^y$  exhibits a nearly ideal behavior at compositions far from the miscibility gap ( $x_2 = 0.6 \text{ mol mol}^{-1}$ ), where it has only a weak composition dependence, and becomes more nonideal toward the miscibility gap ( $x_2 \rightarrow 0.1 \text{ mol mol}^{-1}$ ). Here, the negative values of  $D_{11}$  at  $x_2 = 0.1 \text{ mol mol}^{-1}$  are within the calculated miscibility gap; that is, they are accompanied by a negative eigenvalue  $\hat{D}_2 < 0$ . This behavior is in agreement with the asymptotic limit for  $x_2 \rightarrow 0$ , where  $D_{11}^y$  must coincide with the binary Fick diffusion coefficient  $D_{13}^{\text{bin}}$ . The same trend applies to the cross coefficient  $D_{12}^y$ , which is almost zero for high toluene content and exhibits large negative values near the miscibility gap; here, cyclohexane diffuses against the concentration gradient of toluene. The sign of the cross coefficients is a result of the order of components; i.e., when the order of components is changed, for example, to cyclohexane–methanol–toluene, the coefficient  $D_{12}^y$  becomes positive, cf. the [Supporting Information](#).

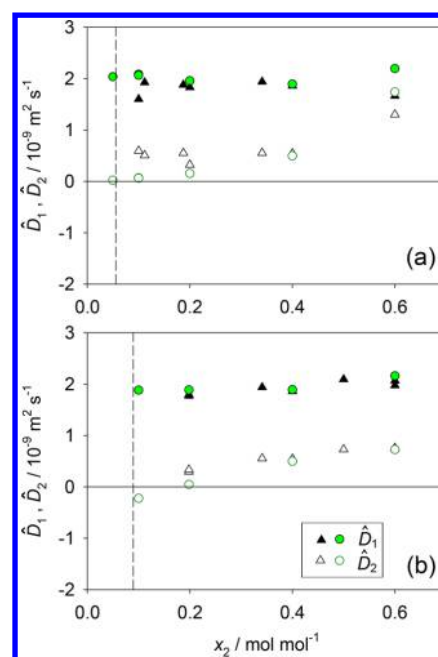
The composition dependence is converse for toluene. Its main coefficient  $D_{22}^y$  and cross coefficient  $D_{21}^y$  are most ideal near the miscibility gap and become nonideal at compositions away from it. At  $x_2 = 0.1 \text{ mol mol}^{-1}$ , the cross coefficient  $D_{21}^y$  is almost zero, which is in agreement with its requirement to vanish at  $x_2 \rightarrow 0$ . It is interesting to note that main and cross coefficients of one component exhibit the same composition dependence in the present case. The asymptotic ternary coefficients are in agreement with the values given by the binary limits, cf. [Figure 5](#). Limiting values at  $x_3 \rightarrow 0$  were also investigated by means of a change of order of components, as presented in the [Supporting Information](#).

To investigate the LLE stability condition toward the miscibility gap, eigenvalues of the Fick diffusion coefficient matrix were calculated along two composition paths at a constant mole fraction of cyclohexane  $x_1 = 0.3 \text{ mol mol}^{-1}$  and methanol  $x_3 = 0.3 \text{ mol mol}^{-1}$ , cf. [Figure 6](#). Consistent with the stability requirement, both eigenvalues are real and positive outside the miscibility gap. While the first eigenvalue exhibits no notable composition dependence along these composition paths, the second eigenvalue approaches zero toward the miscibility gap. This asymptotic behavior of the predicted Fick diffusion coefficient matrix is governed by the thermodynamic factor matrix, for which the determinant must be zero at the spinodal. Because the utilized  $g^E$  model parameters provide a too wide miscibility gap, the predicted second eigenvalue of the Fick diffusion matrix for  $x_3 = 0.3 \text{ mol mol}^{-1}$  becomes already zero slightly outside of the experimental miscibility gap.

## CONCLUSION

Different diffusion coefficient types of the highly nonideal ternary mixture cyclohexane–toluene–methanol were studied. The intradiffusion and Maxwell–Stefan diffusion coefficients were sampled over the entire composition range by equilibrium molecular dynamics simulation. It was found that the intradiffusion coefficients show only a weak composition dependence and are not affected by the nonideality of the present mixture. The intradiffusion coefficient of methanol can be related to the hydrogen-bonding behavior of this species.

The Maxwell–Stefan diffusion coefficients exhibit a pronounced composition dependence. The strongest nonidealities occur for  $\hat{D}_{13}$  and  $\hat{D}_{23}$  in the limit of the according binary subsystems. In the limits  $x_n \rightarrow 0$ , all three sampled ternary



**Figure 6.** Eigenvalues of the Fick diffusion coefficient matrix of cyclohexane (1)–toluene (2)–methanol (3) at a constant mole fraction of cyclohexane  $x_1 = 0.3 \text{ mol mol}^{-1}$  (a) and at a constant mole fraction of methanol  $x_3 = 0.3 \text{ mol mol}^{-1}$  (b). The dashed line delimits the experimental miscibility gap. Simulation results (circles) are compared with experimental data (triangles).

coefficients  $\hat{D}_{ij}$  are in good agreement with the binary coefficients  $\hat{D}_{ij}^{\text{bin}}$ . It was found that none of the available models, which relate MS coefficients to intradiffusion coefficients, are capable of covering the strongly nonideal behavior of MS coefficients as predicted by present EMD simulation work.

In the next step, the thermodynamic factor was obtained from a modified Wilson  $g^E$  model to predict Fick diffusion coefficients. Here, the results are very sensitive to the utilized model and its parameters. With  $g^E$  model parameters fitted only to binary VLE and LLE data, Fick diffusion coefficients were predicted, which are in excellent agreement with experimental literature data. These coefficients were found to satisfy all restrictions imposed by the asymptotic behavior toward the binary limits as well as the stability criterion.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.iecr.8b04385](https://doi.org/10.1021/acs.iecr.8b04385).

Details on equations for different transport diffusion coefficients, reference frame transformation, asymptotic behavior toward binary limits, relations between diffusion coefficients, tested predictive model, utilized  $g^E$  model, hydrogen-bonding statistics, simulation setup, and numerical simulation results ([PDF](#))

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### Notes

The authors declare no competing financial interest.



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